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13. ABSTRACT (Maximum 200 words) The design and operation of a novel forced flow reactor for synthesizing nanocrystalline, high surface area (210 - 250 m ² /g) TiN powders is described. A key in tailoring the characteristics of the powder produced in the reactor is the use of a microwave-generated plasma. Sintering results demonstrate the tremendous potential for pressureless sintering of monodisperse, high surface area nitride powders as well as highlight the need for processing which addresses the proclivity for oxidation of these materials.				
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"Nanocrystalline Processing and Interface Engineering of Si₃N₄-based Nanocomposites"

Technical Report on ONR Grant No. N00014-95-1-0626
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TiN Synthesis and Sintering

This quarter's efforts focused on the synthesis and sintering of TiN. Lessons learned in working in this system and handling these powders will be invaluable to us in our work with nanocrystalline Si₃N₄. Due to its hardness and wear resistance, TiN is potentially very useful in demanding engineering applications. However, due to low sintering activities in microcrystalline powders, TiN has been primarily used as a coating, rather than a monolithic ceramic material. The ultrafine TiN particles synthesized to date (1 - 2) are typically sized over a fairly broad range (10 - 1000 nm) and possess corresponding surface areas of 20 - 60 m²/g. Due to sintering kinetics considerations, the optimum powders for densification should be monosized, such that all the pores are the same size and may disappear simultaneously during sintering. Additionally, as the driving force for sintering is the reduction of surface energy, a high surface area starting powder is desirable. This report outlines a synthesis technique by which such nanocrystalline TiN powders may be produced and presents sintering results using these materials.

A schematic of the current status of our novel reactor for synthesis of nanocrystalline TiN is shown in Figure 1. A He gas stream (3.0 slm), flows over the crucible where Ti is evaporated at $T \geq 2200$ °C. A vacuum pumping system ($P = 2$ mbar) removes the evaporated particles in the He flow from the growth zone over the evaporation source. A mixture of N₂ (2.28 slm) and Ar (0.330 slm) is injected into the He gas stream 0.1 m downstream of the evaporation source. The gas mixture and entrained particles enter a microwave plasma applicator (ASTEX 2110/PA38) operating at 700 W where the N₂ in the gas mixture is dissociated to provide a source of nitrogen radicals for reaction with the Ti clusters. The particles are collected downstream on the chilled (-20 °C) walls of the reactor and on a liquid N₂ cooled disc mounted parallel to the gas flow. Following a synthesis run, the reactor is controllably backfilled with air and the particles are scraped and collected. TiN can be made with and without the plasma applicator in operation.

The starting powders were dried (150 °C, 1.33×10^{-3} mbar) and pressed (200 MPa) in an evacuable pellet die. After cold isostatic pressing (300 MPa), the pellets were ramped under vacuum (2×10^{-2} mbar) at 2 °C/min to 800 °C. The furnace atmosphere was then switched to a 0.1 MPa overpressure of flowing N₂, and the pellets were ramped at 2 °C/min to the sintering temperature for a 30 minute soak.

Characterization of the nanocrystalline TiN powders was performed by nitrogen adsorption (Micromeritics ASAP 2000) and transmission electron microscopy (TEM) (JEOL CX, 200 kV). Chemical analysis for bulk oxygen content was performed by inert gas fusion (LECO TC136). X-ray diffraction (XRD) (Siemens D5000) with Ni-filtered

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Cu-K α radiation was used to determine the phases present and the crystallite size (using the Scherrer formula). The microstructure was examined via scanning electron microscopy (SEM) (JEOL 6320 FE, 3-15 kV). Hardness testing (LECO DM400) was done with a load of 300 gf.

The black TiN particles produced with the microwave plasma (Figure 2a) had an average TEM size of 8.8 nm and B.E.T. surface areas ranging from 210 - 250 m²/g. These surface areas for TiN are the highest reported values that we are aware of in the current literature. The only phase detected in XRD was TiN (crystallite size = 8.6 nm). The lattice parameter was determined to be 4.238 Å (vs. a JCPDS #38-1420 value of 4.2417 Å). The oxygen content of the powders was 15 - 20 wt%.

There was no significant differences in the B.E.T. surface area (~230 m²/g), XRD phase (TiN only), and XRD crystallite size (9.1 nm) of the TiN particles produced without the microwave plasma (Figure 2b). However, as shown in Figure 2, there were very dramatic differences in the degree of aggregation of the particles produced with (WM) and without (WOM) the microwave plasma. The WM particles consist primarily of aggregates of ≤ 100 particles, while the WOM particles consist of very large particle aggregates linked by chains of other particles. Another significant difference is in the particle size distributions shown in Figure 3. While the average TEM particle size of the WOM particles (6.6 nm) is smaller than that of the particles made with the plasma, the distribution is broader. The WM particle size distribution reflects the narrow, log-normal distribution typically found in the inert gas condensation process and is that conducive to high sintering activities. It appears that the microwave plasma has introduced a greater degree of uniformity to the synthesis process. The effectiveness of the microwave plasma in greatly reducing particle agglomeration during synthesis is likely due to one or more of three possible phenomena: the oscillations of the applied field, charging of the particles in the microwave field, and/or the natural convection created by the hot plasma and the cold reactor walls. The high temperature of the plasma likely accounts for the slightly higher average particle size of the WM particles.

The results of pressureless sintering of the TiN powders are shown in Figure 4. The nano-TiN sinters to much higher densities than the conventional TiN (H.C. Starck Grade B, particle size 1.3 - 1.9 μ m, B.E.T. surface area of 2 m²/g). As would be expected due to its characteristics, the WOM powder demonstrates a poorer sinterability at 1400 °C. The fact that the highest densities achieved with the WM powder are somewhat lower than the theoretical density of TiN (~5.35 g/cm³) and the drop in density at 1600 °C are both related to the development of a second phase at higher sintering temperatures. As the nano-TiN is sintered, a Ti₃O₅ phase is crystallized. This phase is first detected by XRD at 1200 °C and has developed appreciably by 1600 °C (Figure 5). While some amount of this Ti₃O₅ is likely present at the grain boundaries, SEM reveals the development of a segregated second phase at 1200 °C. At 1400 °C, a significant amount of this second phase is developed and is shown by EDAX to be enriched in O₂ relative to the primary TiN phase. It seems likely that the large amount of O₂ present on these powders (due to their extremely high surface areas) segregates and crystallizes into this Ti₃O₅ phase at elevated temperatures. As this phase has a lower density (~4.10 g/cm³) than TiN, the overall theoretical density of these materials is lowered. Additionally, substantial cracking at the phase interfaces, likely due to thermal and lattice mismatch between the two phases, occurs at 1400 °C. By 1600 °C, this segregation and cracking have developed to the extent that the density drops significantly. Other work on nano-TiN has also demonstrated the development of small amounts of an O₂-rich second phase upon sintering (2), but our results, due to our higher surface area powder, demonstrate very clearly the oxidation challenge that must be overcome for the successful utilization of high quality, nanocrystalline nitride materials. Despite the cracking, the samples sintered at 1400 °C appear by SEM to be ~95% dense.

The Vickers hardness of these materials (1600 kg/mm²) reflects the crack porosity and the presence of the softer, second phase. Nanocrystalline TiN would appear to have the potential for demonstrating excellent mechanical properties combined with low-temperature sinterability if oxidation can be avoided in powder handling or if its surface oxide layer can be removed via pre-sintering processing. Further studies are underway to examine these issues. A valved filter collection device is being added to the reactor to allow powder removal without exposure to air.

Summary

New experiments with our reactor have utilized the microwave plasma to improve powder characteristics and to synthesize extremely high surface area (210 - 250 m²/g) TiN. The enhanced sinterabilities of these powders, as well as the need to address the oxidation tendencies of nano-nitrides, has been demonstrated.

References

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2. T. Rabe and R. Wäsche, Ceram. Trans. 51, 793 (1995).

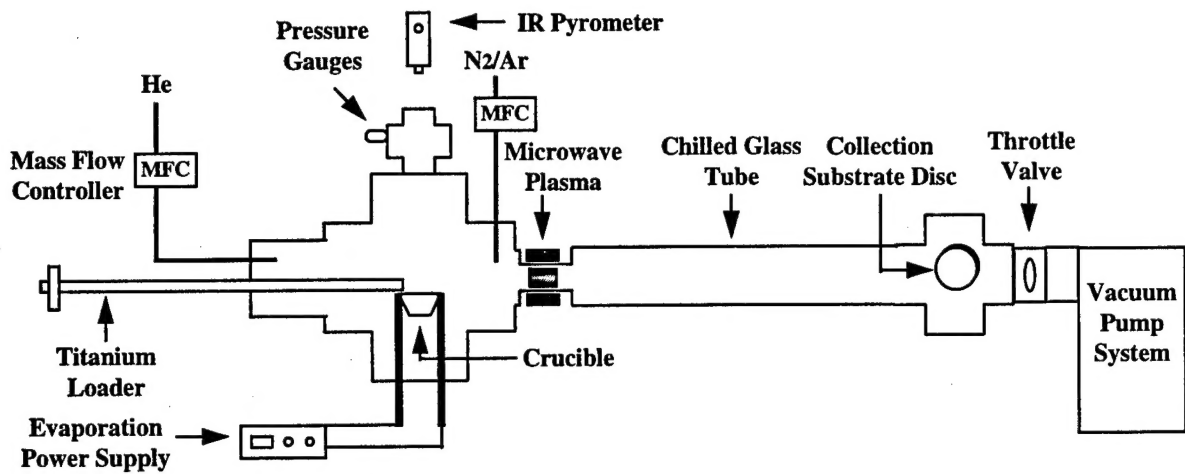


Figure 1: Schematic of forced flow reactor for synthesis of nanocrystalline TiN.

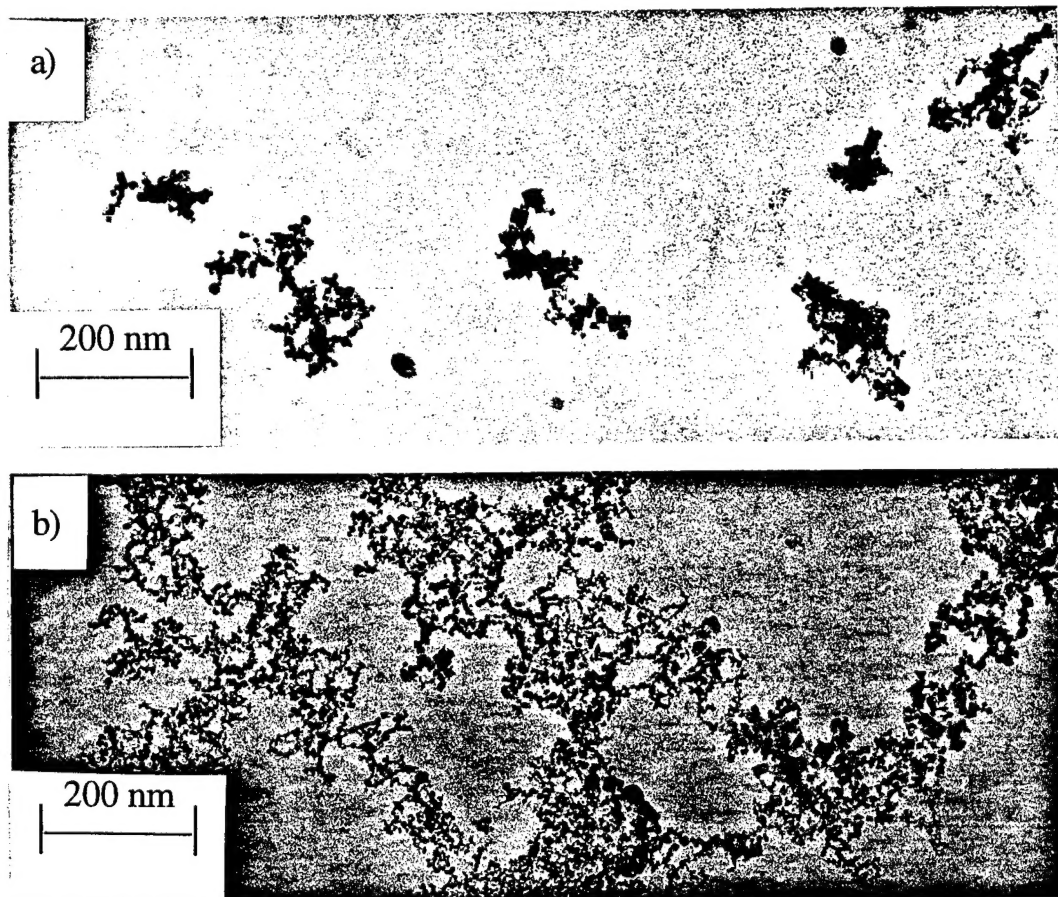


Figure 2: Nanocrystalline TiN particles produced a) with a microwave plasma and b) without the microwave plasma.

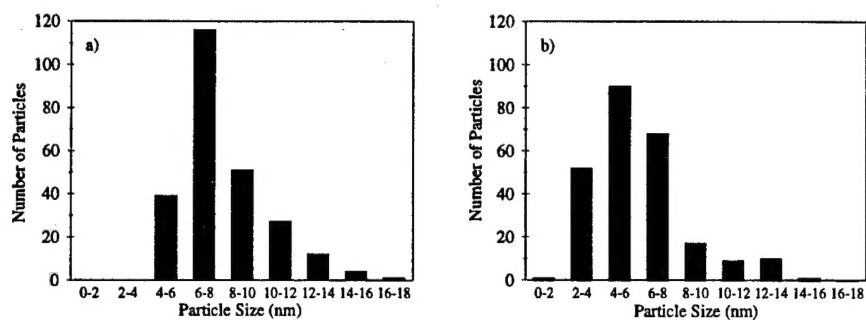


Figure 3: Particle size distribution for TiN produced a) with a microwave plasma and b) without the plasma.

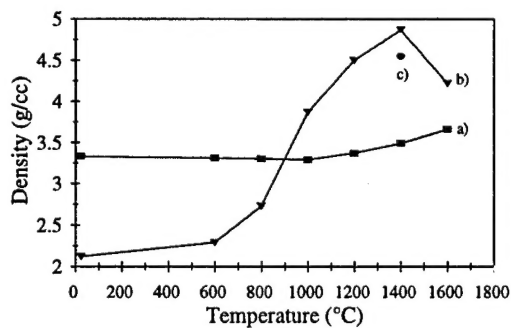


Figure 4: Densification vs. temperature for sintering of a) commercial TiN, b) nano-TiN synthesized with and c) without microwave plasma.

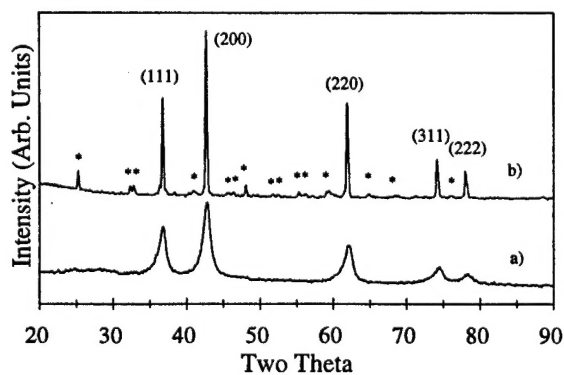


Figure 5: XRD of as-prepared TiN (indexed peaks) and b) TiN sintered at 1600 °C showing development of Ti₃O₅ (*).